Published in *Mat. Sci. Forum* , 239-241, 501-504 (1997)

SPECTROSCOPIC DETERMINATION OF THE EXPECTED OPTICAL COOLING OF YTTERBIUM-DOPED GLASS

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Keywords: laser cooling, absorption, fluorescence, rare earth ions, fluoride glasses

Abstract

The absorption and fluorescence spectra of ZBLANP + 1 wt% Yb^{3+} are measured from 2 to 300 K. From these data, the laser cooling powers at anti-Stokes pump wavelengths can be calculated. In the absence of nonradiative heating, a short, unshielded sample of this glass is predicted to cool with an efficiency of 0.2% at RT relative to the single-pass incident optical power at a wavelength of 1015 nm.

Introduction

Not long after the discovery of anti-Stokes fluorescence, it was recognized that this process can in principle lead to cooling of a material if nonradiative de-excitation is negligible [1-3]. The discovery of the laser led to a renewed interest in the idea [4] and a group at Bell Labs achieved a reduced-heating effect in a sample of Nd^{3+}:YAG by driving the 1.064 μm laser transition in reverse [5]. The first demonstration of net cooling by anti-Stokes emission was accomplished by pumping the 10.6 μm transition of low-pressure CO_2 gas [6]. More recently, several groups have been attempting to cool solvated laser dyes [7,8] and GaAs heterostructures [9] by optically exciting the electronic transitions in their long-wavelength tails.

The first observation of actual cooling of a solid was reported last year [10]. A 0.7-cm long sample of a heavy-metal-fluoride glass doped with Yb^{3+} was cooled by 0.3 K starting from RT. While small in magnitude, this temperature drop corresponds to a cooling efficiency of ~2% relative to the absorbed power, which is sufficient for practical applications if comparable efficiencies are maintained down to about liquid-nitrogen temperatures. In order to explore this issue here, the absorption and fluorescence spectra of ZBLANP:Yb^{3+} are measured between 2 and 300 K. These data permit a determination of the predicted cooling power for a given optical path length as a function of temperature. In turn, the temperature drop of a sample of known dimensions and doping concentration can be calculated for any given initial temperature.

Experimental Results

A commercial sample of ZBLANP (ZrF_4–BaF_2–LaF_3–AlF_3–NaF–PbF_2) glass doped with ultrapure YbF_3 was examined for bubbles, cut, and polished by hand to optical smoothness using non-aqueous compounds. The piece was suspended in a temperature-controlled helium-immersion cryostat with optical access provided for both transmission and 90° scattering measurements. Temperatures as low as 2 K could be obtained by pumping the liquid-helium reservoir down to 20 torr. The sample could be moved out of the optical beam in order to measure the background absorption and scattering.

Trivalent ytterbium has only two $4f$ multiplets, arising from spin-orbit splitting of the lone hole in the valence shell. The ground (excited) state is $^2F_{7/2}$ ($^2F_{5/2}$) and the interaction with the neighboring host atoms in this amorphous material splits these multiplets into 4 (3) levels, leaving only the Kramers degeneracies. The dipole-forbidden $4f \rightarrow 4f$ transition between these two multiplets at around 1 μm is made optically active by a slight admixture of the high-lying $5d$ states; this results in a long radiative lifetime of ~2 ms for $^2F_{5/2} \rightarrow {}^2F_{7/2}$ relaxation [11].

Transmission spectra of the sample were measured from 850 to 1100 nm using a Cary 17 spectrophotometer. The wavelength accuracy of the machine was determined to be about ±0.5 nm using narrow bandpass filters. The spectra were corrected for reflection losses and converted to absorption coefficients, α, using the measured sample length, L, and are plotted in Fig. 1. Three distinct peaks are

apparent and are mainly due to transitions out of the 0" level, as identified in the level diagram. At low temperatures the peaks are inhomogeneously broadened Gaussians; with increasing temperature, phonon dephasing and thermalization [12] smear the lines together. The sharpest peak at all temperatures is the 0"→0' transition; its resolution-deconvolved FWHM varies between approximately 3.7 nm at 2 K and 6.4 nm at 300 K, while the peak wavelength of 975.0 nm shifts by no more than 0.5 nm, which is the limit of accuracy of the measurements [13]. The intensites of the 3 labeled peaks increase by ~30% upon cooling from 300 to 2 K, at the expense of the long-wavelength tail in the spectra which principally represents absorption out of the 1" and 2" levels. The integrated intensity of the entire spectrum is found to be temperature independent to within 5%, which implies that the cross sections for absorption out of the various ground-state levels must be nearly identical. In contrast, typical oscillator strengths for the various crystal-field transitions of a given rare-earth-doped glass vary by up to a factor of 5 [11].

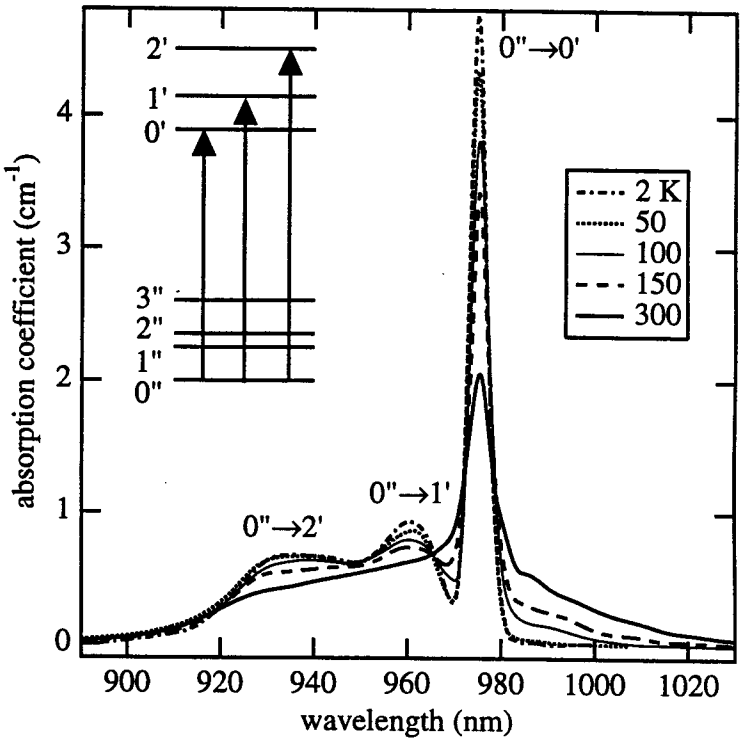

Figure 1. Absorption spectra of ZBLANP + 1 wt% Yb^{3+} at 2 nm resolution.

Ytterbium emission spectra were measured at the same temperatures as were the absorption spectra. A cw argon-ion-pumped titanium-sapphire laser beam was focused onto the sample and the fluorescence was collected at 90° to eliminate the transmitted laser light; the small scattered component was subtracted out of the spectra. Reabsorption of the emitted light was minimized by adjusting the path of the laser beam so that it lay just below the surface from which the fluorescence was collected. This line image was chopped and focused onto the entrance slit of a 1-m monochromator having a 600 lines/mm grating blazed at 1.6 μm. A thermoelectrically-cooled InGaAs detector was used to measure the signal, which was analyzed using a lock-in amplifier. The wavelength reading of the monochromator was calibrated using a low-pressure mercury vapor lamp and is accurate to at least ±0.5 nm; the responsivity of the grating/detector combination was mapped out as a function of wavelength using a blackbody standard source.

The fluorescence spectra are presented in Fig. 2 for a pump wavelength of 960 nm. The integrated intensity is, as in the absorption case, found to be conserved (to within the experimental uncertainty of 25%) as a function of temperature. This result appears to be at odds with the measured temperature dependence of the overall decay rate [14], from which it has been interpreted that the radiative lifetimes, and hence the emission cross sections, for the 3 excited levels are different by at least a factor of 2. Four peaks can be discerned in Fig. 2 and are mostly due to transitions out of the 0' level, as sketched in the level diagram. The dominant 0'→0" peak has the same center wavelength as in absorption, namely 975.0 nm, shifting by no more than 0.5 nm with temperature. Above 100 K, the shape of the spectra are independent of the pump wavelength. At lower temperatures, however, the spectral shapes noticeably depend upon the laser wavelength—at 2 K, the largest shift is seen for the peak at 994 nm, which changes by up to 40% in intensity and 7 nm in wavelength. Given that only the subset of Yb^{3+} ions having transition frequencies resonant with the laser line are excited, such a pump wavelength

dependence would arise if the energy migration to the unexcited, nonresonant centers is slower than the 2 ms radiative decay time [11]. (Note that nonresonant energy transfer is phonon assisted and hence temperature dependent.) An alternative explanation, that the 0' and 1' levels do not fully thermalize prior to the relaxation, seems unlikely [15].

Predicted Cooling

Previously, photothermal deflection spectroscopy has been used to establish that the radiative quantum efficiency for relaxation from the $^2F_{5/2}$ to the $^2F_{7/2}$ manifolds is at least 0.997 [10]. This implies that nonradiative decay, such as by multiphonon relaxation and by energy transfer to or direct laser absorption by impurities, is negligible. In that case, a photon is emitted for each one absorbed. On average, the emitted photons have some energy E_F. This energy corresponds to a wavelength λ_F which can be computed from the measured fluorescence intensities, I_λ, as

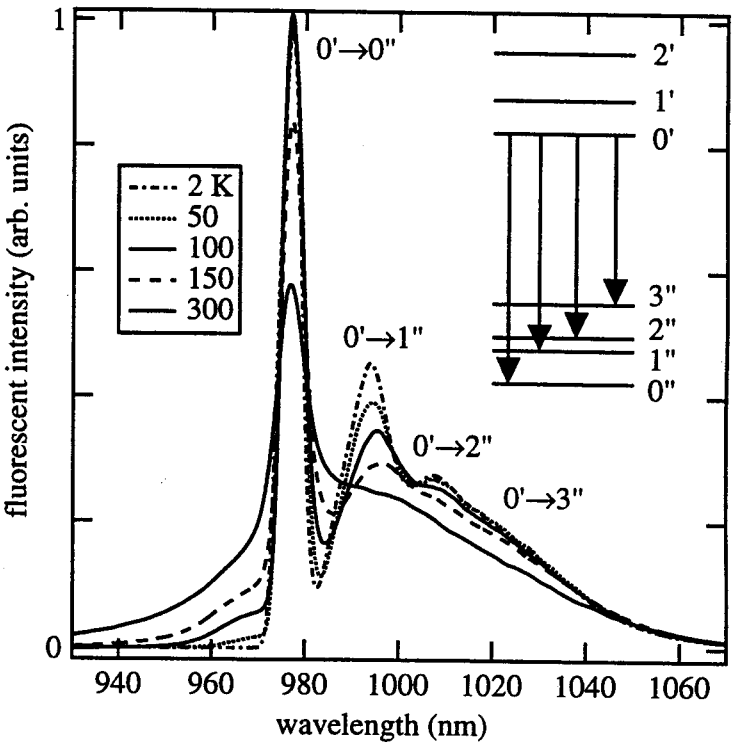

Figure 2. Fluorescence spectra with 0.65 nm resolution of ZBLANP + 1 wt% Yb^{3+} excited at 960 nm.

$$\lambda_F = \left[\int I_\lambda \, d\lambda\right]\left[\int \lambda^{-1} I_\lambda \, d\lambda\right]^{-1}. \tag{1}$$

The resulting values of λ_F for each temperature measured here are tabulated in the inset of Fig. 3 with estimated uncertainties of 2 nm. At 2 K, λ_F is found to vary by about 2 nm as the pump wavelength is tuned across the absorption band, and at 50 K about 1 nm of variation is found; for these two cases, the tabulated values are for long-wavelength pumping, as is relevant to optical cooling.

Now suppose that a sample of ZBLANP:Yb^{3+} is optically pumped with light having a wavelength λ which is longer than λ_F. Then, the emitted power is on average larger than the absorbed power; the fluorescence is shifted up in frequency by the absorption of phonons in the host. As a result, the glass cools—it is easy to see that the cooling power, P_{cool}, is related to the absorbed laser power, P_{abs}, by

$$P_{cool} = P_{abs}(\lambda - \lambda_F)/\lambda_F = P_{inc}(1 - e^{-\alpha L})(\lambda - \lambda_F)/\lambda_F, \tag{2}$$

where P_{inc} is the incident laser power. Thus, the optical cooling power can be calculated as a function of temperature for a given pump wavelength, laser power, and sample length, by interpolating the absorption coefficients from Fig. 1. The results for one choice of parameters are presented in Fig. 3.

Using Eq. 2, the equilibrium temperature, T_S, of a laser cooled sample with surface area A can be calculated for a given heat load. For example, if the dominant heat load, P_{heat}, is blackbody radiation from the environment at ambient temperature T_A, then

$$P_{heat} = \sigma A\left(T_A^4 - T_S^4\right) \approx 4\sigma A T_A^3 \Delta T, \tag{3}$$

assuming that the emissivity of the sample is unity. By equating the right-hand sides of Eqs. 2 and 3, the sample's temperature change ΔT is obtained. An interesting sample geometry is an optical fiber, because it has a large length-to-surface-area ratio; in particular $A \cong \pi DL$, where D is the diameter of the fiber. Using a short piece of fiber, so that the attenuation of the pump beam is minimal along its length at cooling wavelengths, one sees that L cancels out between the two equations. Solving exactly for the

case of T_A = 300 K, D = 250 μm, and P_{inc} = 1 W, a temperature drop of 39 K is predicted. The actual temperature change is expected to be lower due to residual impurity heating, as observed previously in these samples [10]. On the other hand, the cooling could be substantially increased by passing the transmitted laser light back through the fiber, by increasing the ytterbium concentration, and by adding thermal shielding around the sample.

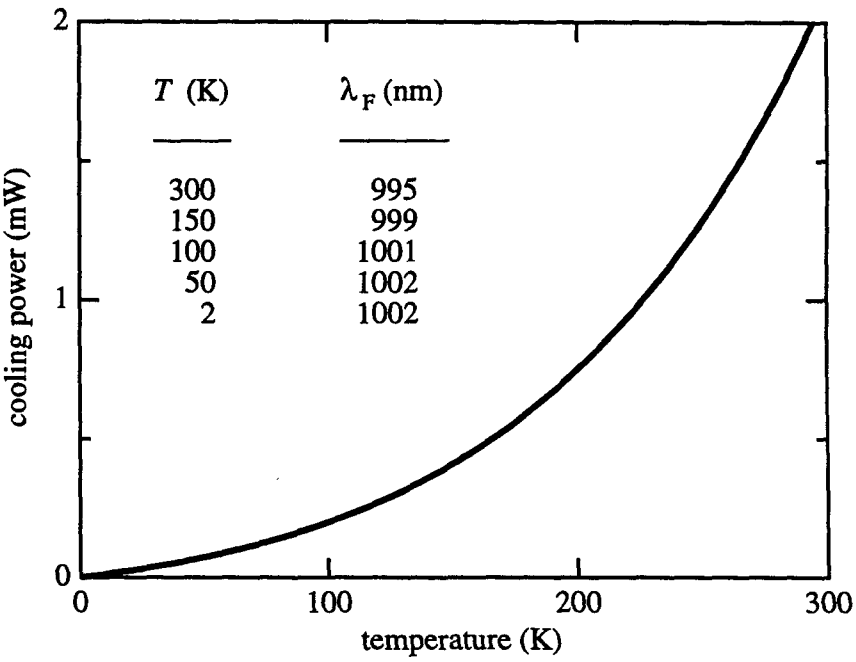

Figure 3. Predicted cooling power upon pumping a 1-cm long ZBLANP + 1 wt% Yb^{3+} sample with 1 W of laser light at a wavelength of 1015 nm.

Acknowledgments

We thank A.J. Gibbs for polishing the sample and M.P. Hehlen for helpful discussions. This work has been supported by the U.S. Department of Energy and by IGPP at LANL.

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[12] For example, level 1' relaxes to 0', which causes broadening; in addition, level 1" becomes populated at higher temperatures, which adds peaks to the spectra.

[13] Also note that the peak absorption coefficient is about twice as large as that of Ref. [10] even though the ytterbium concentration is nominally identical. This may indicate that the Yb^{3+} ions are not homogenenously distributed throughout the quenched castings.

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